

Fatty Acid Amides. V.¹ Preparation of N-(2-Acetoxyethyl)-amides of Aliphatic Acids

BY EDWARD T. ROE, THOMAS D. MILES AND DANIEL SWERN

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In a continuation of our studies on amides of fatty acids, we became interested in N-(2-acetoxyethyl)-amides. The only compound in this class previously described is N-(2-acetoxyethyl)-acetamide, prepared by treating ethanolamine with acetic anhydride² or with ketene.³ When we attempted to prepare it by a slight modification of the former method we obtained diacetamide.

N-(2-Hydroxyethyl)-amides were acetylated (97–99%) by heating with a 100% excess of acetic anhydride for six hours. During the initial stages the temperature rose exothermically to 85–95° after which it was readily controlled at 75°. Careful control to prevent temperatures above 75° resulted in incomplete acetylation. Reactions carried out at 100° for three hours gave lower yields and undesirable side products.

described.⁴

Preparation of N-(2-Acetoxyethyl)-amides.—These amides were prepared by heating one mole of the N-(2-hydroxyethyl)-amide with two moles of acetic anhydride for six hours in a nitrogen atmosphere. During the initial stages the temperature rose exothermically to 85–95° after which it was readily controlled at 75°.

After the acetylation of N-(2-hydroxyethyl)-acetamide, the reaction mixture was distilled at 100 mm. to remove excess acetic anhydride and acetic acid formed. The pressure was then lowered to 5 mm. and the N-(2-acetoxyethyl)-acetamide was distilled. The acetic anhydride and acetic acid were removed similarly from the N-(2-acetoxyethyl)-caproamide reaction mixture, but in this case the crude amide remaining was crystallized five times from a mixture of equal portions of ether and petroleum naphtha, 3 ml./g. at –20°.

N-(2-Acetoxyethyl)-lauramide, -palmitamide and -stearamide reaction mixtures were repeatedly washed by vigorous mechanical stirring with hot water until acid-free. The acetoxyethyl amides were allowed to solidify and the cakes were dried and crystallized: N-(2-acetoxyethyl)-lauramide, once from acetone, 5 ml./g., at 0°, once from ethanol, 10 ml./g., at 0° and once from ether, 12 ml./g., at 24°; N-(2-acetoxyethyl)-palmitamide, once from ethanol, 8 ml./g., at –20°; N-(2-acetoxyethyl)-stearamide, twice from ethanol, 8 ml./g., at –20°.

TABLE I

N-(2-ACETOXYETHYL)-AMIDES OF ALIPHATIC ACIDS

N-(2-Acetoxyethyl)-	Reaction product		Yield, %	M.p., °C.	Crystallized product				Nitrogen, %		Saponification No. ^a	
	Yield, %	M.p., °C.			Carbon, %	Hydrogen, %	Nitrogen, %	Saponification No. ^a	Calcd.	Found	Calcd.	Found
Acetamide ^b	71 ^c	49.6	49.8	7.64	7.35	9.65	9.33	386.5	393.8
Caproamide	99	<24	62	26.5–27.4	59.7	59.5	9.52	9.75	6.96	6.87	278.8	277.1
Lauramide	97	65.1–66.0	30	70.0–70.5	67.3	67.2	11.0	10.7	4.91	5.01	196.6	193.8
Palmitamide	99	78.4–79.0	95	79.5–80.0	70.3	70.8	11.5	11.7	4.10	4.08	164.3	164.5
Stearamide	99	83.1–84.0	92	84.1–84.4	71.5	72.0	11.7	11.7	3.79	3.82	151.8	151.8
Oleamide	99	34.5–35.2	77 ^d	39.0–39.3	71.9	71.9	11.2	11.0	3.81	3.83	152.6	153.3

^a Refluxed 1/2 hour with 0.2 N KOH. ^b Reference 3 gives b.p. 147–154° (8 mm.); n_D^{25} 1.4511; d_4^{25} 1.1015. ^c Distilled once through a 3' Vigreux column; b.p. 142.0–142.5° (5.1 mm.); n_D^{25} 1.4500. ^d Iodine number; calcd. 69.1; found 70.0.

Experimental

Starting Materials.—The N-(2-hydroxyethyl)-amides were prepared from pure fatty acids by refluxing 1 mole of the acid with 1.5 moles of ethanolamine for two to six hours.⁴ N-(2-Hydroxyethyl)-acetamide, b.p. 145–146.7 (2.5 mm.) and n_D^{25} 1.4709, was distilled through a 3-foot Vigreux column. N-(2-Hydroxyethyl)-caproamide was freed of excess ethanolamine by vacuum distillation and then crystallized from ethyl ether, 4 ml./g., at 0° until pure. N-(2-Hydroxyethyl)-lauramide, m.p. 88.0–88.5°, -palmitamide, m.p. 98°, and -stearamide, m.p. 102°, were crystallized directly from the crude reaction mixtures using 95% ethanol, 4 ml./g., at 0°, 10 ml./g. at 0°, and 8 ml./g. at 25°, respectively. N-(2-Hydroxyethyl)-oleamide has already been

The crude reaction mixture of N-(2-acetoxyethyl)-oleamide was dissolved in approximately ten times its volume of petroleum naphtha and washed repeatedly with warm water until free of acid. The petroleum naphtha was then distilled off under vacuum and the residue of crude amide was crystallized twice from ethanol, 10 ml./g., at –20°.

Results are summarized in Table I.

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(1) For Paper IV, see *J. Am. Oil Chemists' Soc.*, **29**, 18 (1952).
(2) S. Fränkel and M. Cornelius, *Ber.*, **51**, 1654 (1918).
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